

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

p.13  
D

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

CN

(11) Publication number:

0 373 800

A1

(2)

## EUROPEAN PATENT APPLICATION

(21) Application number: 89312565.8

(51) Int. Cl.5: A61L 27/00, A61F 2/32,  
C08L 23/06

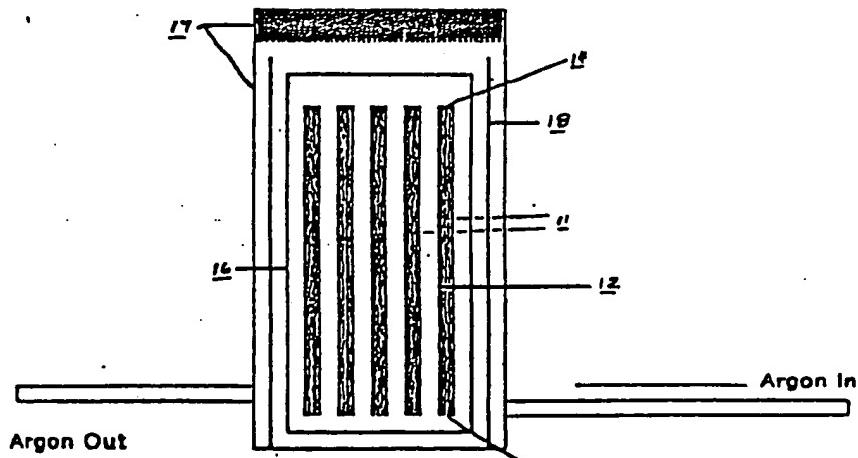
(22) Date of filing: 01.12.89

(30) Priority: 02.12.88 US 278913  
22.12.88 US 288577  
24.10.89 US 426916(71) Applicant: E.I. DU PONT DE NEMOURS AND  
COMPANY  
1007 Market Street  
Wilmington Delaware 19898(US)(43) Date of publication of application:  
20.06.90 Bulletin 90/25(72) Inventor: Howard, Edward George, Jr.  
844 Old Public Road  
Hockessin Delaware 19707(US)(84) Designated Contracting States:  
GR(74) Representative: Jones, Alan John et al  
CARPMAELS & RANSFORD 43 Bloomsbury  
Square  
London, WC1A 2RA(GB)

(54) Ultrahigh molecular weight linear polyethylene, articles and processes of manufacture.

(57) Novel ultrahigh molecular weight linear polyethylene (UHMWLPE) in the form of a shaped article, exhibiting a unique combination of properties making the material useful as a bearing surface, in general, but particularly useful as a prosthetic hip joint cup and as other prosthetic shapes for replacement of other joints of the human body. A novel process for preparing this article is also disclosed.

## FIGURE 1



EP 0 373 800 A1

**ULTRAHIGH MOLECULAR WEIGHT LINEAR POLYETHYLENE, ARTICLES AND PROCESSES OF MANUFACTURE**

**CROSS-REFERENCE TO RELATED APPLICATION**

This application is a continuation-in-part of U.S. Serial No. 07/426,916 filed October 24, 1989 which in  
 5 turn is a continuation-in-part of U.S. Serial No. 07/288,577 filed December 22, 1988, which in turn is a continuation-in-part of U.S. Serial No. 07/278,913 filed December 2, 1988.

**BACKGROUND OF THE INVENTION**

10

**1. Field of the Invention**

This invention relates to a novel ultrahigh molecular weight linear polyethylene (UHMWPE). This novel  
 15 UHMWPE, in the form of a shaped article, exhibits in various embodiments a unique combination of properties making the material useful as a bearing surface, in general, but particularly useful as a prosthetic hip joint cup and as other prosthetic shapes for replacement of other joints of the human body.

20

**2. Description of the Prior Art**

In U.S. Patent No. 3,944,536 (March 1976), Lupton et al describe UHMWPE in the form of a fabricated article exhibiting an elastic modulus of 340,000 to 500,000 psi, a tensile impact strength of 140 to 600 ft  
 25 lb/in<sup>2</sup>, a density of 0.95 to 0.98 g/cc at 25°C, a crystalline melting point of 142 to 148°C (as measured by differential thermal analysis) and a unique crystalline form characterized by the absence of fold spacings of 50-2000 Angstrom units (Å) and the presence of crystal spacings of about 10,000 Å. The critical feature of the process of producing this UHMWPE is disclosed to involve inducing crystallization of the molten polymer above 150°C by rapidly increasing the applied pressure from an initial level of 1 to 1000  
 30 atmospheres to a second level of 2000 to 7000 atmospheres and then cooling rapidly while maintaining a pressure sufficient to maintain the polyethylene in the solid phase until the temperature is below the crystalline melting point of the polyethylene at atmospheric pressure.

In Kunststoffe German Plastics 77 (1987) pp. 617-622, in an article entitled "Ultrahigh Molecular Polyethylene for Replacement Joints", Eyrer et al. point out that the service life of joint replacements made  
 35 of UHMWPE is limited. Analysis of the damage to over 250 explanted hip cups and tibial plateaus revealed a changed property profile which they explained by post-crystallization resulting from oxidative chain decomposition. They suggested optimizing the processing of polyethylene under higher pressure and higher temperature to increase the degree of crystallinity. The Eyrer et al. product displays a creep of above 5% at a compression of 1000 psi (6.9 N/mm<sup>2</sup>) for 24 hours at 37°C.

40 One of the most remarkable advances in the medical field in recent years is the development of prosthetic joints, particularly the load bearing hip. The crippled and sometimes bed ridden elderly can walk again. The key to this development is UHMWPE because, not only does it have the necessary impact strength, but it initiates no adverse blood reactions. But at present, these prosthetic joints are limited to the older, less active segment of the population because the polymer tends to creep under the pressure that a  
 45 younger more active person might develop while involved in recreation or employment. The creep would cause the loss of the close tolerance required between the plastic socket and the polished metal ball attached to the femur. These changes in dimensions disturb the distribution of walking forces which in turn accelerates more creep and wear. Eventually the increased pain requires a traumatic revision operation. One objective of this invention is to provide UHMWPE prosthetic joints with improved creep resistance  
 50 hence removing some of the age restriction existing on the present polyethylene joints.

**SUMMARY OF THE INVENTION**

The object of this invention is to provide a tough UHMWLPE composition and article with creep resistance that is less than 1% (as measured at a temperature of  $23 \pm 1^\circ\text{C}$  and a relative humidity of 50 ± 2% for 24 hours under a comparison of 1000 psi) and that maintains excellent tensile and flexural properties.

5 Specifically, the product of this invention is a composition exhibiting an elastic or flexural modulus of 250,000-500,000 psi, a tensile stress at yield of 3500-4500 psi, a tensile stress at break of 4000-9000 psi, a tensile modulus of 300,000-700,000 psi, preferably 300,000-600,000 psi, an elongation of 200-500%, a notched Izod impact resistance of 12-25 ft. lb. per in. of notch, a creep at a compression of 1000 psi of less than 1% after 24 hours at a temperature of  $23^\circ\text{C}$  and a relative humidity of 50%, the polyethylene having a 10 molecular weight of 1,000,000-10,000,000 (the molecular chain length between folds being greater than 3500Å), a single crystalline melting point of greater than  $144^\circ\text{C}$  (as measured by differential scanning calorimetry) the reduction in said melting point upon reheating being greater than  $11^\circ\text{C}$  above that of the starting polymer and an infrared crystallinity index of at least about 0.45, preferably at least 0.5. The composition may be formed into an article.

15 The process for obtaining the article of this invention involves six (6) important steps:

1. forming, by milling or casting or the like the article from UHMWLPE having a molecular weight of 400,000-10,000,000, preferably at least 1,000,000 and most preferably at least 6,000,000;

2. placing the article in a pressure vessel (e.g. an autoclave) substantially filled with a fluid that is inert to the article, preferably water;

20 3. heating the vessel to a temperature of at least  $190^\circ\text{C}$ , preferably  $200^\circ\text{C}$ - $230^\circ\text{C}$ , and raising the pressure in the vessel, usually by adding additional water, to at least 2800 atmospheres (ATM), preferably at least 3000 ATM;

Alternately, the article, water, and reactor are heated to about  $200$ - $230^\circ\text{C}$ , the pressure is applied and the system held at this temperature while polymer slowly loses heat of crystallization and solidifies.

25 Also, the pressure can be applied at any temperature during the heating cycle if the temperature exceeds about  $200^\circ\text{C}$ .

4. maintaining the temperature and pressure substantially as selected in step 3 for at least 0.5 hour, preferably at least one hour;

30 5. thereafter, cooling by reducing the temperature to a temperature at least below about  $160^\circ\text{C}$ - $170^\circ\text{C}$  preferably to  $160^\circ\text{C}$  or below, most preferably below  $140^\circ\text{C}$ , while maintaining a pressure of at least 2800 ATM preferably at least 3000 ATM, at a slow rate, the rate of cooling being such that temperature gradients in the shaped article are substantially avoided. The polymer must be cooled slowly at the high pressure until it is fully crystallized. At 3000 ATM pressure, the crystallization temperature of UHMWLPE of over one million molecular weight is in the range of  $170^\circ\text{C}$ - $190^\circ\text{C}$ . The pressurized vessel 35 should be cooled slowly to insure that the temperature of the polymer is not significantly above the vessel temperature, particularly if the pressure vessel construction does not permit means for measuring the temperature of the polymer itself.

35 6. cooling and releasing the pressure on the shaped article in a manner such that any remelting of the article is prevented. This is accomplished by cooling at least to a temperature below the atmospheric pressure melting point, i.e., about  $130^\circ\text{C}$ - $135^\circ\text{C}$  preferably below  $120^\circ\text{C}$ , most preferably below  $100^\circ\text{C}$  and releasing the pressure to reduce it from at least 2800 ATM to approximately 1 ATM, either sequentially or simultaneously. It should be understood that it is necessary to cool the polymer to a temperature below its melting point at any particular pressure to ensure that none of the polymer melts as the pressure is reduced since lowering the pressure lowers the melting point.

40 45 As an optional seventh step, it is advisable to shave the surface of the article, i.e. remove approximately the outer 2 millimeters that might contain any fluid-affected polymer.

A very important step is the fifth step, i.e. cooling in a manner that limits severe temperature gradients in the article. For example, for a 1 inch X 6 inch rod, a cooling rate of approximately  $10^\circ\text{C}$  per hour is usually necessary. Although cooling rates no greater than  $10^\circ\text{C}$  per hour are preferred, cooling rates as 50 high as about  $35^\circ\text{C}$  per hour have been used to provide the product of this invention. However, these latter rates require careful control in order to limit temperature gradients during cooling. Cooling rapidly, as taught in the prior art, will not provide the article of this invention. This invention is particularly useful for manufacturing shaped articles where temperature gradients pose a problem during the cooling step, i.e., where the article's cross-sectional dimensions are at least 1 inch x at least 1 inch, usually for joints at least 55 1 inch x at least 2 inches. Specifically, the importance of this step and of this invention is manifest in producing articles having as its smallest dimension 0.2 inch, i.e., at least 0.2 inch in thickness. It has been found that in such articles, the temperature gradients must still be controlled by the process of this invention in order to obtain the product of this invention.

Alternately, for steps 2 and 3, the pressure vessel can be used more efficiently by preheating polymer outside the reactor because heating polyethylene is a very slow process due to its high heat of fusion and its thermal insulation property. It can be heated in an oven, preferably in an inert atmosphere to prevent oxidation, particularly when the temperature is above 160 °C. Because the UHMW polyethylenes do not flow when melted, they can be handled while hot and transferred to the preheated pressure vessel without deforming.

Product resulting from this modified process also is excellent for orthopedic replacement and has certain superior characteristics. Values demonstrating these superior, enhanced qualities are shown in Example 11.

10 In addition to utility in the field of orthopedic replacement, the products prove useful in other applications also requiring the special properties of the products. Not only shaped articles are of interest, but also films and fibers as well as other "downstream" forms and unshaped granular forms of the product will prove useful. Film formed of the product of Example 5 is exemplified in Example 13. These examples are illustrative only, and other forms, shaped and unshaped, of the composition are contemplated within the scope of the invention. Therefore, "article" shall include both shaped articles and unshaped articles.

15 In a process more recently developed for manufacturing the product of this invention, the fluid used in the pressure vessel could be a gas that does not affect the UHMWLPE adversely. Specifically, the shaped article is formed from commercially available UHMWLPE. In the second step, the article is placed in a pressure vessel containing the fluid, in this case argon. However, it is necessary in the case where argon is used, to protect the UHMWLPE from any entry of the gas into the polymer by surrounding the article with a thin stainless steel or similar metal can as described in copending U.S. Patent Application (DE-0289C) filed to S. Li on November , 1989 which is a continuation-in-part of U.S. Serial No. 07/426,918 filed on October 24, 1989 which in turn is a continuation-in-part of U.S. Serial No. 07/288,576 filed December 22, 1988 which in turn is a continuation-in-part of U.S. Serial No. 07/278,912 filed on December 2, 1988. It should be understood that other gaseous fluids may be used in place of argon. So long as the gas does not adversely affect or is prevented from adversely affecting the polymer and is not affected by the temperatures and pressures used in the process, the gas may be used.

20 In the next step, a pressure of at least 2800 ATM is applied and the vessel is heated to about 220 °C for about 6 hours. Thereafter, the temperature is "ramped" down at a rate no greater than about 10 °C per hour to about 160 °C while maintaining the pressure above 2800 ATM. The temperature is then "ramped" down at a maximum rate to 50 °C while maintaining the high pressure, after which the pressure is released.

25 A further embodiment of the invention involves the following important steps:

30 1. forming by milling a casting or the like, the article from UHMWPE having a molecular weight of 400,000-10,000,000, preferably at least 1,000,000;

35 2. subjecting said article to a temperature of 190-340 °C, preferably 320-340 °C, for at least 0.5 hour, preferably at least one hour, in an inert atmosphere; and

40 3. cooling the article non-precipitously to a temperature of at 130 °C or below. As in the other embodiments, the rate of cooling is such that temperature gradients in the shaped article are substantially avoided. Again, the rapid cooling sought in the prior art will not provide the article of this embodiment. The product of this non-pressurized embodiment is particularly useful for manufacturing shaped articles where temperature gradients pose a problem during the cooling step, i.e., where the article's cross-sectional dimensions are at least 1 inch x at least 1 inch, usually for joints at least 1 inch x at least 2 inches. Specifically, the importance of this step and of this invention is manifest in producing articles having as its smallest dimension 0.2 inch, i.e., at least 0.2 inch in thickness.

45 For purposes of this invention, ultrahigh molecular weight linear polyethylene (UHMWLPE) is defined as a linear polyethylene having an estimated weight-average molecular weight in excess of about 400,000, usually 1,000,000 to 10,000,000 as defined by a melt index (ASTMD-1238) of essentially zero and a reduced specific viscosity (RSV) greater than 8, preferably 25-30. The relationships of RSV to intrinsic viscosity and to molecular weight are those developed by R. Chaing as presented by P. S. Francis et al. in 50 J. Polymer Science, 31, 453 (1958).

It is envisioned that the modifications of adding a preliminary step heating the product to 320-340 °C will also provide superior characteristics to the product described by Li.

The improved properties of the products of this invention in its various embodiments are reflected in a tensile modulus of at least 300 kpsi, a flex modulus of at least 250 kpsi, ultimate tensile strength greater than 4000 psi, yield strength greater than 3500 psi and an elongation at break no greater than 500%.

A very important property of the product of this invention is its creep resistance. For prosthetic devices, e.g. knee, hip, elbow joints, etc., any substantial creep can be devastating in the loss of the benefits of extremely expensive surgery. Thus, the shaped articles of this invention display as little as a 0.5% loss in

thickness when subjected to a compression pressure of 1000 psi for 24 hours at a temperature of 23° C and a relative humidity of 50% in accordance with ASTM D-621.

- For some applications, still lower creep, higher stiffness, higher elongation, and particularly higher tensile strengths at yield are necessary. These can be introduced by the enhancing process if the polyethylene is first thermally heated at 320-340° C for thirty minutes or longer. The process depends on heating the polymer as near as possible to, without reaching, its decomposition point. The hot polymer should be cooled slowly because very rapid cooling, such as immersion in cold water, causes internal voids to form. This is caused by the combination of large volume changes polyethylene undergoes when melting (about 30%) and its poor heat conductivity. A convenient method is to allow the polymer to cool wrapped in insulation. The hot polyethylene can be put directly into the hot pressure vessel or it can be cooled and reheated to the normal 200° C in the pressure vessel.

The improved properties of the product of this part of the invention are reflected in tensile modulus of at least 350 kpsi, a tensile strength at yield of 3500-5400 psi, and a creep value of less than 0.6%.

- In addition, the thermally heated polymer, still in the folded chain form used to make this superior form of this invention, in itself has improved elongation, crystallinity, and impact resistance over the starting material, but it is not equivalent to the enhanced form of polyethylene.

Perhaps the most characteristic property of the product of this invention is its infrared crystallinity index (IRCI). This property, which provides a reasonably accurate reflection of the crystallinity of this material, is in a range never before attained with any UHMW polyethylene materials. To determine this index, samples are first obtained by microforming thin sections. Heat and pressure should be avoided during preparation of the samples. IRCI is the ratio of the band at 1894 reciprocal centimeters ( $\text{cm}^{-1}$ ) to the band at 1305 reciprocal centimeters ( $\text{cm}^{-1}$ ). Since the band at 1894  $\text{cm}^{-1}$  is attributed to the crystalline nature of the material and the band at 1305  $\text{cm}^{-1}$  is attributed to its amorphous nature, IRCI increases as the crystallinity increases. The product of this invention displays an IRCI of at least about 0.45. In fact, values of 0.73 and higher have been obtained. On the other hand, IRCI values for prior known UHMWLPE's seldom reach above 0.3.

The invention will be more clearly understood by referring to the drawings and examples, which follow. In the drawings, Figure 1 is a schematic diagram of the equipment used in the process for forming the product of the invention using argon gas; and Figure 2 is a schematic diagram of the equipment used in the hydrostatic process.

In the examples, most of the properties are measured using standard ASTM tests.

All of the physical measurements were carried out under constant humidity (50% relative humidity) and temperature (23° C) conditions.

Tensile modulus, ultimate tensile strength, yield strength and elongation were measured according to ASTM D-638 with the following modifications:

- samples machined into shape without lubricating fluid
- type I tensile bar
- cross head speed 0.2"/min for tensile modulus
- 2.0"/min for tensile stress and elongation.

Creep resistance was measured in accordance with ASTM D-621 with the following modifications:

- samples machined into cylinders or cubes without the use of lubricating fluids
- samples measured 0.5" x 0.5" x 0.5"

Flexural properties were measured according to ASTM D-790 with the following modifications:

- samples machined into shape without the use of lubricating fluids
- 45 • typical flex bar measures 0.125" thick x 0.5" width x 5" length
- span or gage is 2.0". (This was determined by a span/depth ratio of 16/1.)
- cross head speed = 0.05"/min (calculated based on span).

Impact resistance was measured using the notched Izod test given in ASTM D-256 with the following modifications:

- 50 • samples machined into shape without the use of lubricating fluid
- type A or notched Izod
- specimen size is 0.5" x 2.5"
- 0.4" from bottom of vertex to opposite side
- 1.25" impacted end (from end of bar to vertex of notch)
- 55 • the notch should be the specified angle of 22.5 degrees.

It should be appreciated that in all embodiments of the invention the step of forming the article by milling, casting, or the like from UHMWLPE may be performed as the first step in the process (i.e., before heating or preheating) or as the last step in the process (i.e., after the cooling step).

The following non-limiting examples, including the improved and superior embodiments, illustrate the basic principles and unique advantages of the present invention. Various changes and modifications may be made without departing from the spirit and scope of the present invention.

5

### EXAMPLE 1

The material used in this example is American Hoechst Hostalen 415 GUR ultrahigh molecular weight polyethylene. It was obtained in the form of bars, 3" in diameter and up to 5' long in length. The material will be referred to as UHMWLPE. The molecular weight was over 1,000,000.

One or more pieces of the UHMWLPE 11 were placed into stainless steel, seamless, 48" long cylinders or sleeves 12. The thickness of the stainless steel was 1/8". The bottom of the cylinders was closed by welding a stainless steel cap 13 onto the bottom of the cylinder. The top of the cylinder was partially closed by welding on a modified cap 14 which contained a vacuum port 15. The cylinder was then evacuated using a vacuum pump and sealed by crimping the port to form a can that surrounds the piece of UHMWLPE completely. The sealed cylinder was then placed in a containment vessel 16 large enough to hold 15 cylinders. The containment vessel 16 was then placed into a hot isostatic pressing (HIP) unit 17 with molybdenum heating units 18. Thermocouples were added to monitor the temperature of the cylinders.

The basic function of the HIP process is to uniformly heat a load while applying pressure uniformly to all surfaces. The pressure medium used in this case was argon. The UHMWPE is protected from contact with the argon by the stainless steel cans.

The process conditions were:

1. Apply pressure to 39,000 psi.
2. Heat to 220 °C.
- 25 3. Hold for 6 hours at 220 °C and a minimum pressure of 41,000 psi (27 atmos.).
4. Ramp temperature down at a rate no faster than 10 °C per hour to 160 °C. Pressure is maintained above 41,000 psi during this time.
- 30 5. Ramp temperature down at maximum rate to 50 °C while maintaining the pressure above 41,000 psi.
6. Below 50 °C, pressure may be let down and the cycle ended.

The UHMWPE rods were then removed from the sleeves and parts were fabricated for physical testing. It is noted that the material produced exhibits much higher tensile modulus, flex modulus, melting point, density and creep resistance than the starting material (Control A).

35

	Material	DSC Melting Point (°C)	Density (grams/cc)	IRCI
40	Control	137.0-140.7 °C	.93-.94	0.24
	Example 1	148.0-152.0 °C	.947	≥ 0.45

45

50

55

	ASTM D638	Control A	Example 1
5	Flex Modulus kpsi	165	291
	Tensile Modulus kpsi	185	315
	Ultimate Tensile kpsi	4500	4688
10	ASTM D638		
	Yield kpsi	3476	4082
	Elongation (break) %	262	227
[values are averages of 5 tests]			
15	ASTM D621 Creep Test		
	Load		
	500 psi	.5	.3 % deformation
	1000 psi	1.6	.7
	2000 psi	5.9	2.4

20 Additional evidence of the products' distinctiveness is found in data produced by small angle X-ray testing. A truly characteristic small-angle X-ray scattering plot of desmeared intensity (by the method of P. W. Schmidt, Acta Cryst., 13, 480 (1960) and Acta Cryst., 19, 938 (1965)) ( $1 \times (2 \text{ theta})$  squared) versus scattering angle (2 theta) for the material of the invention exhibits two distinct scattering peaks associated with crystal long-spacings in the range of 480 angstroms (at 2 theta = .184 degrees) and 4610 angstroms (at 2 theta = .0192 degrees). The presence of the sharp diffraction peak at the lower angle is indicative of an extended polymer chain conformation (with a lamellar thickness greater than 2000 angstroms) whereas the more diffuse higher-angle peak corresponds to a lamellar thickness characteristic of conventional folded chain PE. This provides clear evidence for the presence of two scattering peaks in the subject invention material which correspond to lamellar thicknesses both above and below 2000 angstroms. By comparison, the previously patented extended chain polyethylene of Lupton et al., was reported to exhibit a complete absence of any detectable small angle X-ray scattering in the range of 50 to 2000 angstroms. Consequently this work demonstrates that the subject invention material is morphologically distinguishable from Lupton et al.

35

#### EXAMPLE 2

40 The material used in this example is an ultrahigh molecular weight polyethylene obtained from Jet Plastics, Inc.

A rod 21 measuring 6" x 1 1/8" was placed in the cavity 22 of a stainless steel, seamless, cylindrical reactor 23. The cavity 22 had a diameter of 1.35" and was about 9" long.

Water was fed into the cavity 22 at the entry port 24 through the use of a high pressure water pump 25 powered by compressed air. Simultaneously, the reactor was heated by electrical heaters 26 surrounding the reactor.

In the first step, the rod 21 was heated to a temperature of 220°C under a hydrostatic pressure of 2000 ATM. The pressure was raised to 3000 ATM while the temperature was maintained at 220°C for 2 hours. The temperature was permitted to fall to 208°C over another 2 hour period, and then to about 182°C in 4 hours. Finally, the rod was cooled to 49°C by subjecting the reactor 23 to compressed air from the blower 27 over a period of one hour and the pressure released.

The rod was removed from the reactor and the surface was shaved. The product, a sample taken substantially from the center of the rod, displayed a DSC melting point of 154.5°C, and, on reheating, a DSC melting point of 140°C.

55 The material, when subjected to a compression pressure of 1000 psi for 24 hours at a temperature of 23°C and a relative humidity of 50% in accordance with ASTM D-621, deformed only 0.4%.

The other properties of the product were:

flexural modulus - over 250 kpsi

tensile modulus - over 300 kpsi

tensile stress (yield) - over 3500 psi  
 tensile stress (break) - over 4000 psi  
 elongation (break) - less than 500%.

Its infrared crystallinity index was over 0.5.

- 5 The hydrostatic process described in Example 2 is the best mode for preparing the product of this invention. This process has important advantages. The pressure transfer liquid, water, is non-toxic and inexpensive. The hydraulic pressure is applied equally in all directions resulting in a substantially homogeneous product. This compares to processes shown in the prior art where hydraulic pressure is applied by a piston or a ram. In these latter cases, the high shrinkage polymer tends to solidify along the heat-  
 10 escaping walls making it difficult for the pistons to advance and still apply the pressure uniformly. The result is a heterogeneous product.

It should be understood that although water is the preferred liquid fluid to use in the process, other liquids, with the same criteria as mentioned for gases, are also useful. Thus, methanol, ethanol, glycerin, glycols, etc. in addition to various aqueous solutions may be used.

- 15 The salt selected for an aqueous solution may be one that imparts a desirable property to the surface of the shaped article.

### EXAMPLE 3

20

This experiment was carried out in a manner similar to Example 2 except that the pressure in the first step was 3000 ATM. The material was maintained at 220 °C under 3000 ATM for 4 hours. The temperature was allowed to fall to 190 °C over an 8-hour period. After which, it was cooled to 100 °C in 1 hour.

- 25 Samples were taken from 1/8" inside both ends of the rod and had melting points of 150.8 °C and 153.2 °C. When reheated, the melting points were 135.5 °C and 138 °C, respectively.

The infrared crystallinity index was 0.791; and the creep, when measured in accordance with ASTM D-621, was less than 1%. These measurements were obtained on a sample taken from the center of the rod.

30

### EXAMPLE 4

- 35 The experiment was also carried out in a manner similar to Example 2 except for the following changes in the heating/cooling cycle:

Heat at 211 °C and 3000 ATM and maintain for 1 hour;

Cool to 200 °C in 1 hour at 3000 ATM;

Cool to 180 °C over 5 hours at 3000 ATM (cooling rate 200→180 °C, 4 °C/hour); and

Cool to 33 °C in 1 hour and 3 minutes.

- 40 The product from inside both ends melted at 150 °C and on reheating, at 135.5 °C. The product, when tested in accordance with ASTM D-621 displayed a creep of less than 1%. Its infrared crystallinity index was 0.652.

45

### EXAMPLE 5

- A reactor with the general configuration shown in Figure 2 having an internal diameter of 4" and being 22" long, was charged with a 3 1/8" x 18 1/16" rod of UHMWPE (made from polymer from American Hoechst, Hostalen GUR 415). The closed vessel was evacuated, filled with water, and heated to 232 °C at which point the pressure was increased to 3000 ATM with the water pump. This pressure was maintained until the end of the experiment. The reactor was held between 210 and 230 °C for 3 hours, cooled over 1 hour to 200 °C, cooled to 175 °C in 5 hours (5 °C/hour) and then cooled to 80 °C in 7 1/2 hours.

The resulting product rod was still in a cylindrical form with very little warpage. It measured 3 1/8" x 17 15/16". End pieces, 1/2" thick, were cut off each end of the rod revealing a uniform white color. Samples taken from the center of the rod on these cuts gave melting points of 152.9 °C (201 J/g) and 152.1 °C (207 J/g) when heated at 20 °C/min. When reheated, the melting points were 137.5 °C.

A six inch section of the rod was sawed into 3/16" thick shapes for physical tests, then carefully milled

to remove saw marks to 1/8" thickness. The resulting polymer had the following properties:

5	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%;">IZOD Flexural Modulus</td><td style="width: 50%;">18.7 ft. lb./in. of notch 298.9 kpsi</td></tr> <tr> <td colspan="2" style="text-align: center; padding-top: 10px;"><b>Tensile Properties</b></td></tr> <tr> <td>Stress at yield</td><td>4190 psi</td></tr> <tr> <td>Stress (max.) (at break)</td><td>5430 psi</td></tr> <tr> <td>Elongation (at break)</td><td>280%</td></tr> <tr> <td>Modulus</td><td>378.3 kpsi</td></tr> <tr> <td>Creep Test, 1000 psi</td><td>0.6%</td></tr> </table>	IZOD Flexural Modulus	18.7 ft. lb./in. of notch 298.9 kpsi	<b>Tensile Properties</b>		Stress at yield	4190 psi	Stress (max.) (at break)	5430 psi	Elongation (at break)	280%	Modulus	378.3 kpsi	Creep Test, 1000 psi	0.6%
IZOD Flexural Modulus	18.7 ft. lb./in. of notch 298.9 kpsi														
<b>Tensile Properties</b>															
Stress at yield	4190 psi														
Stress (max.) (at break)	5430 psi														
Elongation (at break)	280%														
Modulus	378.3 kpsi														
Creep Test, 1000 psi	0.6%														
10	All tests at room temperature.														
15	The crystallinity index (IRCI) was 0.528.														

20

EXAMPLE 6

In this example, the product was prepared with an exceedingly smooth surface.

25 A polished brass disk, about 1 1/2" diameter, 1/4" thick was pressed at 160°C against a UHMW polyethylene plug. The combination was cooled under pressure and sealed in a heat shrinkable Teflon FEPTM tube. The polyethylene was converted in a hydrostatic system by this procedure in the vessel used in Example 5.

The heating, cooling cycle was as follows:

- 3000 ATM and 210°C in 1 hour;  
 30 3000 ATM 210°C to 200°C in 1 hour;  
 3000 ATM 200°C to 178°C in 6 hours, 45 minutes;  
 and  
 3000 ATM 178°C to 23°C in 2 hours, 20 minutes.

35 The polyethylene did shrink so that it had a smaller diameter than the disk, but the polymer stuck to the surface. When forced apart, the surface was extremely smooth.

This technique is important in preparing complicated surfaces where smoothness is extremely important, such as on bearing surfaces such as medical prosthesis for knee and hip joints, or bearings for motor shafts, etc. Machine cutting polymers always leaves very small ridges.

40

EXAMPLE 7

45 The reactor of Figure 2, internal diameter 4" by 22" long was charged with a 3" x 18" rod of American Hoescht, Hostalen GUR 415 ultrahigh molecular weight polyethylene, water, and a nominal pressure of 100 psi. The system was heated to 170°C to 176°C and held there for 1 hour, then the pressure was raised to 3000 ATM. The temperature was maintained at 179°C-174°C for 3 hours, during which time the polyethylene crystallized. The reactor was cooled to 79°C in 1.7 hours.

50 Two samples were taken; one from the center of the rod and another 1/2 inch from the outer surface of the rod. The melting points, as measured by DSC, were 150.9°C and 150.4°C, respectively, and upon reheating, 136.6°C and 137.3°C. Thus, the increases in melting points were 14.3°C and 12.7°C, respectively. The infrared crystallinity index was 0.5.

55

EXAMPLE 8

This example shows that the polymer can be cooled at a rate as high as 34.5°C per hour in the critical

cooling step (step 5) if proper precautions are taken to limit temperature gradients.

A one inch rod of UHMWLPE from Jet Plastics, Inc. was used. It was placed in the pressure vessel with water and subjected to the following treatments:

- 3000 ATM and 220 °C for 2 hours;
- 5 3000 ATM, cool to 200 °C in 50 minutes;
- 3000 ATM, cool to 177 °C in 40 minutes;
- 3000 ATM, cool to 35 °C in one hour.

A test sample taken one-half inch from the end of the rod and in the center displayed a DSC melting point of 153.8 °C, and, on reheating a DSC melting point of 139.7 °C.

- 10 The material, when subjected to a compression pressure of 1000 psi for 24 hours at 23 °C and a relative humidity of 50% in accordance with ASTM D-621 deformed 0.5%.

#### EXAMPLE 9

15

Superior Enhanced UHMW Polyethylene prepared by Preheating Polymer to 325 °C.

- 20 A 3-1/16" x 15" rod of UHMW polyethylene (Hoechst GUR415, fabricated by PolyHi) was heated to 325 °C in an atmosphere of N<sub>2</sub> for six hours. The hot rod was quickly placed in a pressure vessel preheated to 212 °C. The vessel was sealed immediately and pressured with water to 3000 ATM. The cooling schedule was as follows:

- 212 °C to 191 °C 65 minutes
- 25 191 °C to 181 °C 63 minutes
- 181 °C to 175 °C 2 hours
- 175 °C to 174 °C 6 hours, 26 minutes
- 174 °C to 45 °C 3 hours, 15 minutes

The rod was cut into test samples and analyzed with the following results:

30

#### DSC (Differential Scanning Calorimetry)

<u>Center of Bar</u>	<u>1 cm from Bar Edge</u>
----------------------	---------------------------

m.p., °C		
1st heat	150.5	152.4
2nd heat	137.9	139.0
ΔT	12.6	13.4

40

#### Heat of Fusion

1st heat	198.8 J/g
2nd heat	134.4 J/g

45

#### Infrared Crystallinity Index

(Samples cut from within 5 mm of bar edge)

In Bar Direction	0.613
Perpendicular to Bar Direction	0.633

50

#### Flex Modulus (KPSI)

424.0

386.1

55

Deformation (Creep) ASTM D621 (% at 1000 psi load)

In Bar Direction 0.4

Perpendicular to Bar Direction 0.6

Density g/ml

Gradient column 0.9595

Infra Red 0.957, 0.958

Tensile Properties:Perpendicular to

In Bar Direction	Bar Direction
(6" Test Bars)	(2-1/2" Test Bars)
<u>(Type I)</u>	
<u>(Type V)</u>	

Tensile Strength, PSI

Yield:	4743	4516
	4758	4526
Max:	4743	5614
	4758	5005
Break:	4396	5004
	3695	5040

Tensile Modulus,

KPSI:	611.1	520.3
	613.0	513.9

Elongation, %:

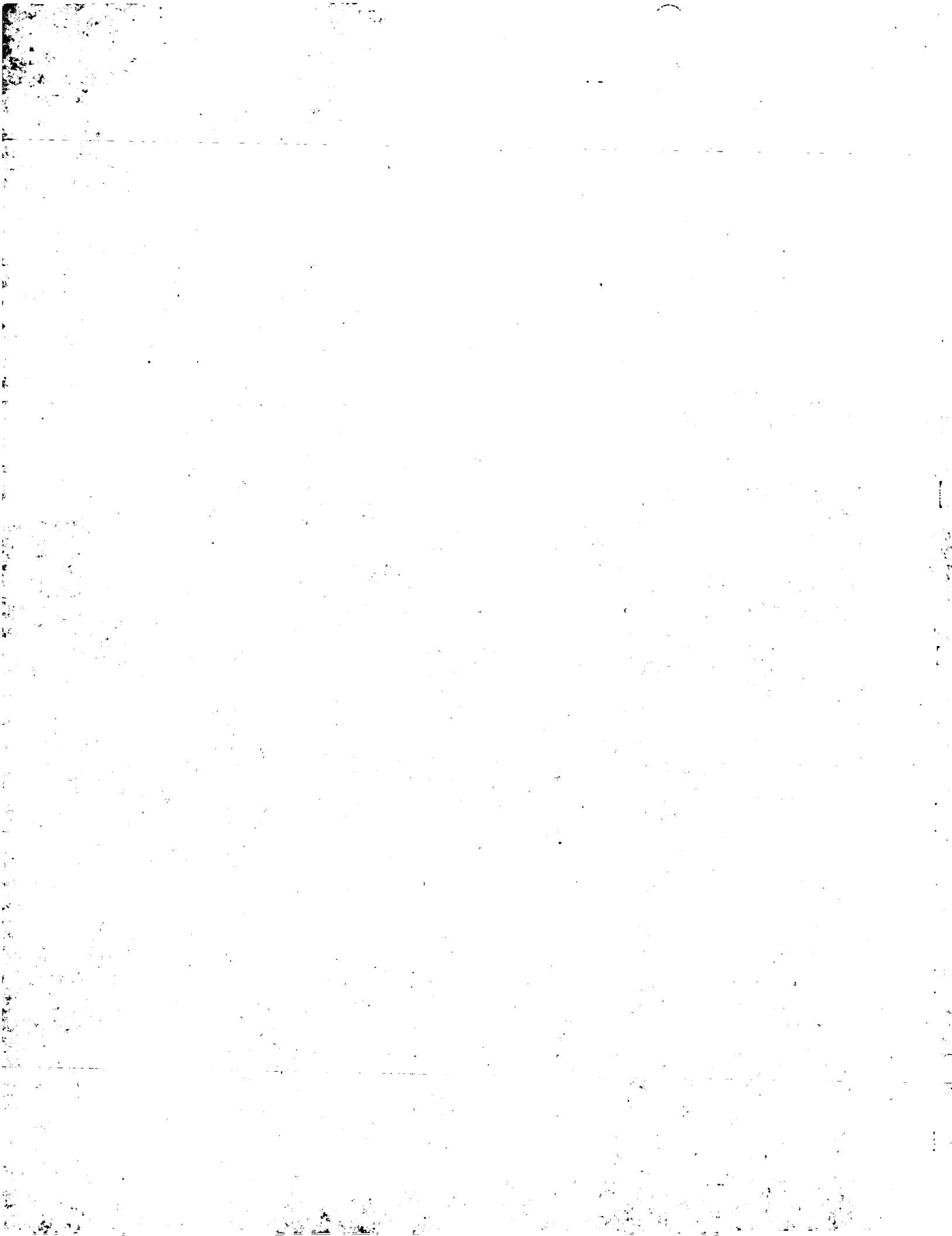
Break	355	433
	315	400

IZOD IMPACT, ft.lb./in. of notchPerpendicular to

<u>Bar Direction</u>	<u>Bar Direction</u>
24.8	26.1
22.0	25.0

EXAMPLE 10

Effect of Sequence of Heat-treatment, Cooling, Reheating to a Lower Temperature, and Pressure Recrystallization on UHMWPE.



- A 3" x 18" rod of UHMWPE (American Hoechst, Hostalen GUR 415) was heated in refluxing vapors of Krytox®-143AZ (E. I. du Pont de Nemours and Company, Wilmington, Delaware) (at 333-335 °C) for 2 hours, 40 minutes. Krytox®-143AZ is a perfluoroalkylpolyether that is a nonflammable, chemically inert liquid having unusually high thermal and oxidative stability. Other materials demonstrating these characteristics may also be suitable. The system was protected by a nitrogen atmosphere and was wrapped with glass insulation to facilitate slow cooling. As compared to the starting material, the resulting product has improved crystallinity (IRCI from 0.27 to 0.47), a tensile modulus (from 210 KPSI to 300 KPSI), and tensile strength at yield (from 3400 to 3850 psi). Most significantly, the product displays a large increase in elongation at break (from 315% to 893%).
- When the above described material was recrystallized from 220 °C under 3000 ATM, a new polyethylene resulted possessing extremely high elongation at break (667%) along with the high tensile strength at yield (4900 psi) and the tensile modulus (574 KPSI) expected of the superior, enhanced UHMWPE materials.

15	Flex Modulus, KPSI	436.4
		431.2
		433.80 (av)
	Density	.9684
20	IZOD IMPACT, (ft.lb./in. of notch)	17.1
		15.9
		16.5 (av)

25

EXAMPLE 11

- Further evidence shows that UHMWPE polymer pretreated to at least 325 °C gives a superior enhanced material (SEUHMW PE).

The purpose of this Example is to show the importance of the preheat temperature.

35	Preheat Temperature(C ° C)	225	290	310	325
	Crystallinity Index	.553	.550	.605	0.76
	Heat of Fusion, J/g	186	200	190	219
	Tensile, Yield PSI	4268	4277	4212	4819
	Deformation (Creep) ASTM D621 Test (% at 1000 psi load)	0.6			0.4
40	IZOD ft.lb./in. of Notch	20.6	20.7	20.6	24

45

Effect of Heating Temperature on UHMW PE

- The samples were heated by placing 3/4" cubes of UHMW polyethylene (Hoechst Hostalen GUR 415, m.w. 4-6 million, fabricated by Westlake) wrapped in Teflon® film in a large test tube protected from air with N<sub>2</sub>. In the first experiment, a small thermocouple was inserted into the center of the cube, the purpose being to determine the time necessary for the sample to reach test temperature. A plug of glass wool was placed above the sample to control convection currents. The tube was heated with a Wood's metal bath. After the heat treatment was complete, the sample was wrapped in insulation to ensure slow cooling. At a bath temperature of 250 °C, the sample required 45 minutes to reach test temperature.

56

	Time Sample at Temperature hrs:min	Test Temperature C	Crystallinity Index (by IR)
5	4:00	250	0.232
	20:00	250	0.244
	4:00	293	0.264
	:01	293	0.230
	4:00*	320-325	0.374
	1:00*	334-335	0.378
	1:00*	340-342	0.391

\*Heated by submerging sample wrapped in Teflon® film under Woods metal as described in the following paragraph.

15

#### Effect of Time on Heating UHMW PE

20

Small cubes (3/4") of UHMW PE cut from the rod form of Hoechst Hostalen GUR 415 were wrapped in Teflon® film, tied to a glass rod, and pushed under the surface of a Wood's metal bath. In the first experiment, a small thermocouple was inserted in the cube. When plunged into a 322-329 °C bath, twelve minutes were required for the sample center to reach 321 °C. The time at temperature (not the time in the bath) is recorded below. The samples were removed from the bath and wrapped in glass fiber insulation to permit slow cooling which required 1.5 hours to reach 80 °C. The extent of change was determined by measuring crystallinity indices.

30

Time Sample (at 320-325 °C (hrs:min)	Crystallinity Index by (IR)
no heating	.258
0:10	.261
0:20	.294
1:00	.330
4:00	.374

40

#### Heat Treatment of UHMW PE (Large Scale)

45

A 3" diameter by 18" bar of UHMW polyethylene (Hoechst Hostalen GUR 415, m.w. 4-6 million, fabrication by Westlake) was heated under nitrogen at 325 °C for 4 hours (65B). The bar was cut into test pieces as was a bar of the same starting polymer that had not been treated. Tests were run sequentially.

50

55

	<u>Untreated</u>	<u>Thermally</u>	%
	<u>Polymer</u>	<u>Treated</u>	<u>Difference</u>
5	<u>DSC</u>		sharper (narrow curve)
10	m.p. °C	139.7	137.5
Heat of			
15	Fusion J/g	154.6	197.5
Crystallinity			+28
Index (IR)	0.258	0.386	+50
20	<u>Tensile Properties</u>		
	<u>Tensile Strength, psi</u>		
25	Yield	3380	3694
		3456	3642
		3418 (av)	3668 (av) +7.3
30	Max.	5361	4706
		4864	4673
		5113 (av)	4690 (av)
35	Break	5361	4705
		4864	4673
		5113 (av)	4689 (av)
40	<u>Elongation, % Break</u>		
		330	490
		300	500
		315 (av)	495 (av) +57
45	<u>Modulus, KPsi</u>	208.4	244.6
		210.5	253.7
		209.5 (av)	249.1 (av) +19
50	<u>Flex Modulus, KPsi</u>		
		124.4	151.5
		137.1	146.8
		130.7 (av)	149.1 (av) +14
55	<u>IZOD IMPACT, (ft.lb./in. of notch)</u>		
		15.93	19.97
		20.81	22.68
		18.37 (av)	21.32 (av) +16

## Deformation (Creep) ASTM D621 Test

5 (% at 1000 psi load)

1.8	1.6	-17
1.7	1.3	

10

Similarly, a 3" diameter bar of different UHMW polyethylene (Hirmont 1900, m.w. 1,000,000) was heat pretreated in an inert atmosphere, for example, of N<sub>2</sub>. The physical properties of the product had greatly improved elongation and impact resistance.

15

	Untreated Polymer	Thermally Treated	% Difference
DSC			
Heat of Fusion J/g	166.3	190.7	+ 15
Crystallinity Index (IR)	.284	.379	+ 33
Tensile Properties			
Tensile Strength, psi			
Yield	3544	3721	
	3703	3589	
Max.	3622 (av)	3655 (av)	- 0
	7387	6545	
	7190	5999	
	7289 (av)	6272 (av)	-14
Elongation, % Break			
% Yield	200	343	
	216	293	
	208 (av)	318 (av)	+ 53
Modulus, KPsi	16.6	20	
	20	16.6	
	128.4	212.7	
	216.2	192.7	
	202.7 (av)	202.7 (av)	0
IZOD IMPACT, (ft.lb./in. of notch)			
	13.05	24.26	
	11.94	17.12	
	12.49 (av)	21.09 (av)	+ 65

45

50

EXAMPLE 12

55 A 3" diameter bar (rod), 18" in length, of American Hoechst Hostalen GUR 415 ultrahigh molecular weight polyethylene, was heated in an oven and then encapsulated with low molecular weight polyethylene by rolling the hot rod onto a 1/16" sheet of low molecular weight polyethylene heated to 180°C on a large hot plate. An intervening sheet of "Teflon" Polytetrafluoroethylene film was kept on the encapsulated rod to prevent sticking to the hot plate. The rod ends were similarly sealed. The "Teflon" film was kept on the encapsulated rod to prevent sticking in the reactor.

The bar was heated to 225°C under a nitrogen atmosphere and transferred to the reactor at 225°C. After sealing, the reactor pressure was taken to 3000 atmospheres which caused the temperature to reach 237°C. The reactor was permitted to cool to 180°C in 6.5 h, then maintained at this temperature for 1h. The temperature was dropped to 170°C, held at this temperature for 3h, then cooled slowly to 150°C from where it was cooled rapidly.

The rod, which remained coated, was cut and machined into two test pieces (A and B) which gave the following results:

		SAMPLE	
DSC		A	B
1st Heat:			
Melt point, °C	149.1	153.7	
Heat of Fusion, J/g	219.8	209.5	
2nd heat:			
Melt point, °C	135.5	136.6	
Heat of fusion, J/g	141.2	144.9	
Crystallinity Index (IR)	0.566	0.567	
Tensile Properties:			
Tensile Strength, psi			
At Yield	4149	4076	
At Max.	7448	8138	
At Break	7448	8138	
Elongation, %	323	346	
Modulus, Kpsi	363.6	358.2	
Creep Deformation, % (D621)	0.6	0.6	
IZOD Impact, (ftlb/in. of notch)	15.9	15.8	

35

EXAMPLE 13

A 5.75" segment of enhanced ultrahigh molecular weight polyethylene prepared as in Example 5, was skived to two films (A and B), of 11 mil and 5 mil thickness, respectively. The following properties were obtained (averaged from five tests per film sample):

		SAMPLE	
		A	B
Tensile Properties:			
Tensile Strength, psi			
At Yield	3035	3108	
At Max.	6554	4083	
At Break	6481	4083	
At 5% Elongation	2667	2705	
Tensile Modulus, Kpsi	129.7	165.6	
Elongation at Break, %	470	237.6	

The skived films were hot drawn in a tenter frame at 140°C. One piece of the 5 mil film was drawn 6

fold in one direction (C). A second piece of the 5 mil film was drawn 3 fold in both directions (D):

	SAMPLE	
	C	D
<b>Tensile Strength, psi:</b>		
At Yield	37,819	13,720
At Max.	42,058	19,358
At Break	46,426	18,995
Tensile Modulus, Kpsi	93.3	94.9
Elongation at Break, %	56	132.4
Thickness, mils	2.6	1.6

15

### CONTROL B

20

In this experiment, a product was prepared in the manner of Example 1 of U.S. Patent No. 3,944,536. A sample of the ultrahigh molecular weight polyethylene used in Example 1 previously described herein, measuring 1/4" x 1/4" x 1/8" thick was heated between a film of polytetrafluoroethylene on a hot plate at atmospheric pressure and at a temperature of 160°C on the upper side and 270°C on the lower side.

The molten sample was transferred quickly to a hydraulic press at room temperature where the sample was subjected to a pressure of 8 tons (about 250,000 psi or about 16,000 ATM). It required 1.6 seconds to attain full pressure. The resulting polymer was tested. It displayed an infrared crystallinity index of 0.199. Its melting point was 134.5°C and, when reheated, 134.4°C.

30

### Claims

- 35 1. An ultrahigh molecular weight linear polyethylene exhibiting a flexural modulus of 250,000-500,000 psi, a tensile stress at yield of 3500-4500 psi, a tensile stress at break of 4000-9000 psi, a tensile modulus of 300,000-700,000 psi, a notched Izod impact resistance of 12-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 0.45.
- 40 2. The composition of Claim 1 wherein the tensile modulus is 300,000-600,000 psi, the notched Izod impact resistance is 12-20 ft. lb. per inch of notch and the infrared crystallinity index is at least 0.5.
- 45 3. The composition of Claim 2 shaped into an article wherein its dimensions are at least one inch by at least one inch.
4. The composition of Claim 2 shaped into an article wherein its smallest dimension is at least 0.2 inch.
5. The composition of Claim 2 wherein its infrared crystallinity index is at least about 0.5.
6. An article consisting essentially of the ultrahigh molecular weight linear polyethylene of Claim 1 exhibiting a flexural modulus of 250,000-500,000 psi, a tensile stress at yield of 3500-4500 psi, a tensile stress at break of 4000-9000 psi, a tensile modulus of 300,000-700,000 psi, a notched Izod impact resistance of 12-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 0.45.
- 55 7. The shaped article of Claim 6 wherein the tensile modulus is 300,000-600,000 psi, the notched Izod impact resistance is 12-20 ft. lb. per inch of notch and the infrared crystallinity index is at least 0.5.
8. The shaped article of Claim 6 wherein its dimensions are at least one inch by at least one inch.
9. The shaped article of Claim 6 wherein its smallest dimension is at least 0.2 inch.

10. The shaped article of Claim 6 wherein its infrared crystallinity index is at least about 0.5.
11. A process for obtaining the ultrahigh molecular weight linear polyethylene of Claim 1 consisting essentially of the following steps:
- (a) forming said article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000-10,000,000;
  - 5 (b) subjecting said article to a fluid under pressure of at least 2800 ATM and a temperature of 190°C-300°C;
  - (c) maintaining the temperature from 190°C-300°C and the pressure of at least 2800 ATM for at least 0.5 hour;
  - 10 (d) reducing the temperature to at least below 160°C-170°C while maintaining the pressure at at least 2800 ATM, the rate of reduction in temperature being such that temperature gradients in the shaped article are substantially avoided; and
  - (e) cooling to a temperature of about 130°C or below and releasing the pressure to approximately 1 ATM in a manner such that remelting of said article is prevented.
- 15 12. The process of Claim 11 wherein step (a) is performed after step (e) is performed.
13. The process of Claim 11 wherein said fluid is water.
14. The process of Claim 13 wherein said pressure in step (b) is at least 3000 ATM.
15. The process of Claim 13 wherein said temperature in step (b) is 200°C-230°C.
16. The process of Claim 13 wherein the temperature and pressure in step (e) is maintained for at least 20 one hour.
- 17. The process of Claim 13 wherein the surface of the article is shaved after step (e).
  - 18. The process of Claim 13 wherein the cooling rate in step (d) is no greater than 35°C per hour.
  - 19. The process as in Claim 13 wherein the cooling rate in step (d) is no greater than 10°C per hour.
  - 20. An ultrahigh molecular weight linear polyethylene exhibiting a flexural modulus of 250,000-650,000 psi, a tensile stress at yield of 3500-5400 psi, a tensile stress at break of 4000-6000 psi, a tensile modulus of 300,000-700,000 psi, a notched Izod impact resistance of 12-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 0.45.
  - 25 21. The composition of Claim 20 wherein the tensile modulus is 300,000-650,000 psi, the notched Izod impact resistance is 12-25 ft. lb. per inch of notch and the infrared crystallinity index is at least 0.5.
  - 22. The composition of Claim 21 shaped into an article wherein its dimensions are at least one inch by at least one inch.
  - 30 23. The composition of Claim 21 shaped into an article wherein its smallest dimension is at least 0.2 inch.
  - 24. The composition of Claim 21 wherein its infrared crystallinity index is at least about 0.5.
  - 25. An article consisting essentially of the ultrahigh molecular weight linear polyethylene of Claim 20 exhibiting a flexural modulus of 250,000-650,000 psi, a tensile stress at yield of 3500-5400 psi, a tensile stress at break of 4000-6000 psi, a tensile modulus of 300,000-700,000 psi, a notched Izod Impact resistance of 12-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 45.0.45.
  - 40 26. The article of Claim 25 wherein the tensile modulus is 300,000-650,000 psi, the notched Izod impact resistance is 12-25 ft. lb. per inch of notch and the infrared crystallinity index is at least 0.5.
  - 27. The article of Claim 26 wherein its dimensions are at least one inch by at least one inch.
  - 28. The article of Claim 26 wherein its smallest dimension is at least 0.2 inch.
  - 50 29. The article of Claim 25 wherein its infrared crystallinity index is at least about 0.5.
  - 30. A process for obtaining the article of Claim 25 consisting essentially of the following steps:
    - (a) forming said article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000-10,000,000;
    - 55 (b) subjecting said article to a preliminary heat treatment at a temperature of between 320-340°C, in an inert atmosphere for at least 0.5 hour;
    - (c) subjecting said article to a fluid under pressure of at least 2800 ATM and a temperature of 190°C-300°C;
    - (d) maintaining the temperature from 190°C-300°C and the pressure of at least 2800 ATM for at

- least 0.5 hour;
- (e) reducing the temperature to at least below 160°C-170°C while maintaining the pressure at at least 2800 ATM, the rate of reduction in temperature being such that temperature gradients in the shaped article are substantially avoided; and
- 5 (f) cooling to a temperature of about 130°C or below and releasing the pressure to approximately 1 ATM in a manner such that remelting of said article is prevented.
31. The process of Claim 30 wherein step (a) is performed after step (f) is performed.
32. The process of Claim 30 wherein said fluid is water.
33. The process of Claim 32 wherein said pressure in step (c) is at least 3000 ATM.
- 10 34. The process of Claim 32 wherein said temperature in step (c) is 200°C-230°C.
35. The process of Claim 32 wherein the temperature and pressure in step (f) is maintained for at least one hour.
36. The process of Claim 32 wherein the surface of the article is shaved after step (f).
37. The process of Claim 32 wherein the cooling rate in step (e) is no greater than 35°C per hour.
- 15 38. The process as in Claim 32 wherein the cooling rate in step (e) is no greater than 10°C per hour.
39. An improved folded chain ultrahigh molecular weight linear polyethylene exhibiting a flexural modulus of 150,000-300,000 psi, a tensile stress at yield of 3500-4000 psi, a tensile stress at break of 4000-6000 psi, a tensile modulus of 150,000-300,000 psi, a notched Izod impact resistance of 15-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 2% after 24 hours at a temperature of 20 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, preferably of at least 1,000,000 and an infrared crystallinity index of at least about 0.35.
40. The composition of Claim 39 wherein the elongation (% at break) is 250-900, the notched Izod impact resistance is 15-20 ft. lb. per inch of notch.
41. The composition of Claim 39 shaped into an article wherein its dimensions are at least one inch by 25 at least one inch.
42. The composition of Claim 39 shaped into an article wherein its smallest dimension is at least 0.2 inch.
43. An article consisting essentially of the improved folded chain ultrahigh molecular weight linear polyethylene of Claim 39 exhibiting a flexural modulus of 150,000-300,000 psi, a tensile stress at yield of 30 3500-4000 psi, a tensile stress at break of 4000-6000 psi, a tensile modulus of 150,000-300,000 psi, a notched Izod impact resistance of 15-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 2% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, preferably of at least 1,000,000 and an infrared crystallinity index of at least about 0.35.
- 35 44. The article of Claim 43 wherein the elongation (% at break) is 250-900, the notched Izod impact resistance is 15-20 ft. lb. per inch of notch.
45. The article of Claim 44 wherein its dimensions are at least one inc' by at least one inch.
46. The article of Claim 44 wherein its smallest dimension is at least 0.2 inch.
47. A process for obtaining the article of Claim 43 consisting essentially of the following steps:
- 40 (a) forming said article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000-10,000,000;
- (b) subjecting said article to a temperature of 190°C-340°C for at least 0.5 hour in an inert atmosphere; and
- (c) cooling the article non-precipitously to a temperature of about 130°C or below.
- 45 48. The process of Claim 47 wherein step (a) is performed after step (c) is performed.
49. The process of Claim 47 wherein said temperature in step (b) is 320°C-340°C.
50. The process of Claim 47 wherein the temperature in step (b) is maintained for at least one hour.
51. A process for producing a superior, enhanced ultrahigh molecular weight polyethylene displaying an elongation at break of at least 400% consisting essentially of the following steps:
- 50 (a) subjecting an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000 to 10,000,000 to a preliminary heat treatment of refluxing vapors at a temperature of between 320-340°C, in an inert atmosphere for at least 0.5 hour;
- (b) subjecting said article to a fluid under pressure of at least 2800 ATM and a temperature of 190°C-300°C;
- 55 (c) maintaining the temperature from 190°C-300°C and the pressure of at least 2800 ATM for at least 0.5 hour;
- (d) reducing the temperature to at least below 160°C-170°C while maintaining the pressure at at least 2800 ATM, the rate of reduction in temperature being such that temperature gradients in the shaped

article are substantially avoided; and

(e) cooling to a temperature of about 130 °C or below and releasing the pressure to approximately 1 ATM in a manner such that remelting of said article is prevented.

5 52. The process of Claim 51 wherein said fluid is water.

53. The process of Claim 51 wherein said pressure in step (b) is at least 3000 ATM.

54. The process of Claim 51 wherein said temperature in step (b) is 200 °C-230 °C.

55. The process of Claim 51 wherein the temperature and pressure in step (e) is maintained for at least one hour.

56. The process of Claim 51 wherein the surface of the article is shaved after step (e).

10 57. The process of Claim 51 wherein the cooling rate in step (d) is no greater than 35 °C per hour.

58. The process as in Claim 51 wherein the cooling rate in step (d) is no greater than 10 °C per hour.

59. The product produced by the process of Claim 51.

15

20

25

30

35

40

45

50

55

FIGURE 1

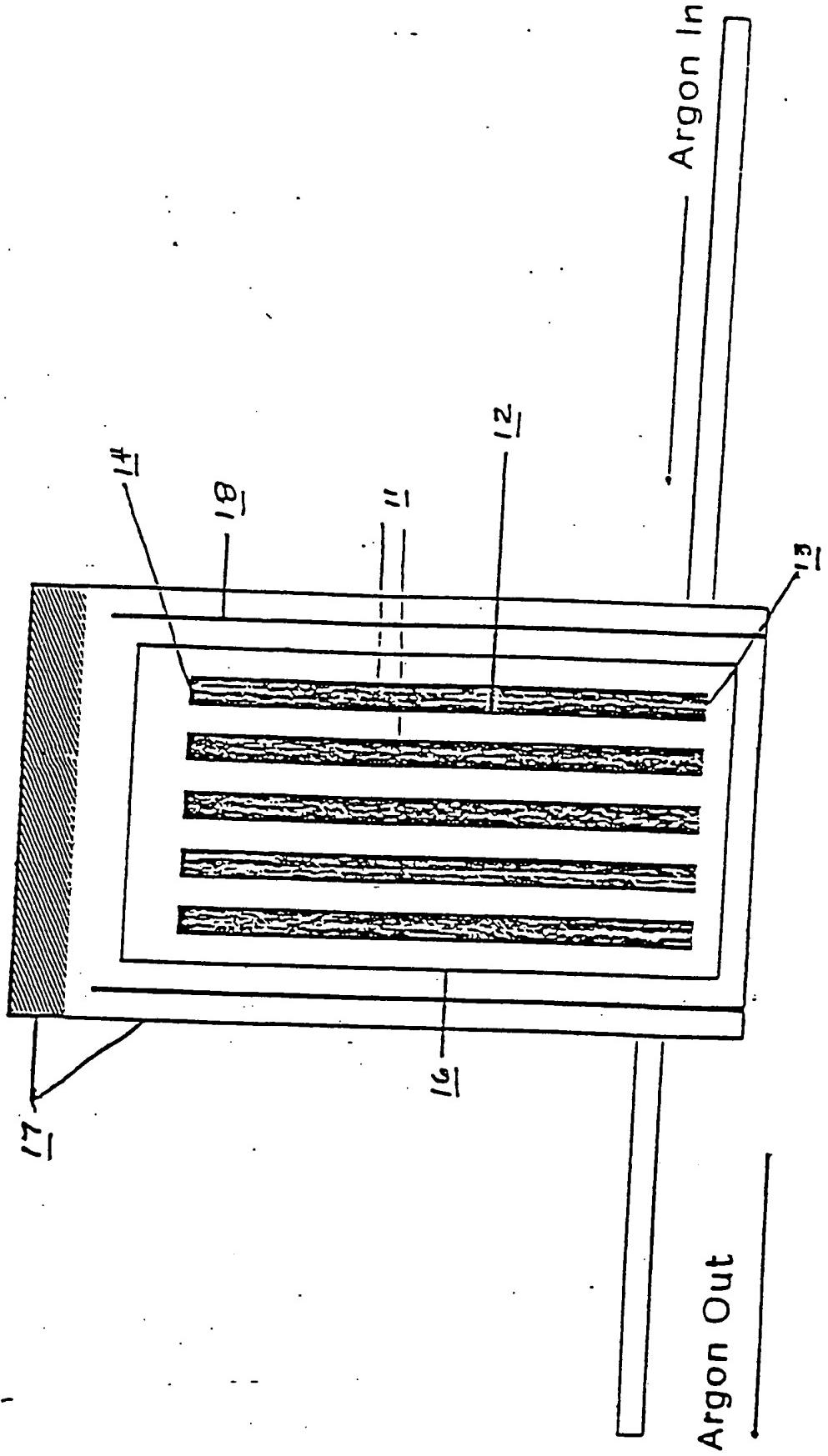
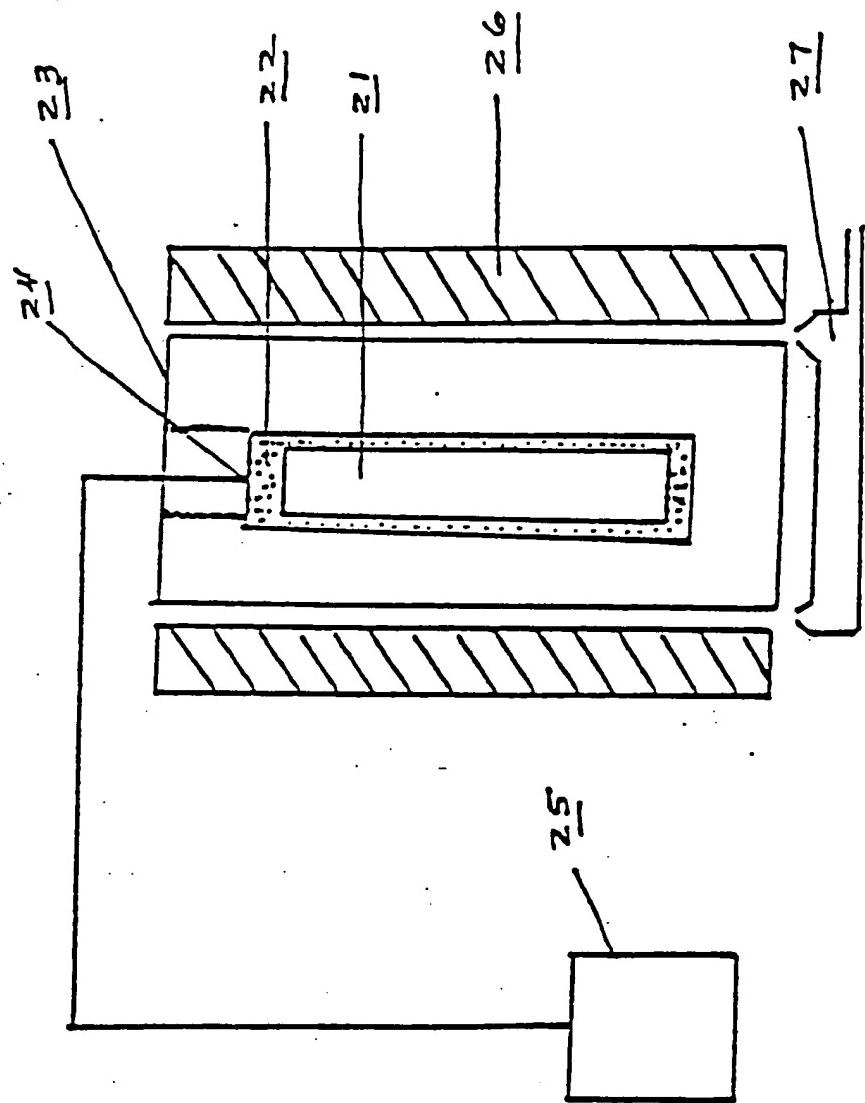


FIGURE 2





EP 89 31 2565

## **DOCUMENTS CONSIDERED TO BE RELEVANT**

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CLS)
A	POLYMER, vol. 22, January 1981, pages 23-28, IPC Business Press, London, GB; BHATEJA: "Uniaxial tensile creep behaviour of ultra high molecular weight linear polyethylene" * Page 28, conclusions * ---	1	A 61 L 27/00 A 61 F 2/32 C 08 L 23/06
A	JOURNAL OF POLYMER SCIENCE: PART A2, POLYMER PHYSICS, vol. 7, 1969, pages 2051-2059, John Wiley & Sons, New York, US; DAVIDSON & WUNDERLICH: "Extended-chain crystals. II. Crystallization of polyethylene under elevated pressure" * Page 2052, lines 32-38 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. CLS)
			A 61 L A 61 F C 08 L
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	29-03-1990	GOOVAERTS R.E.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date		
A : technological background	D : document cited in the application		
O : non-written disclosure	L : document cited for other reasons		
P : intermediate document	& : member of the same patent family, corresponding document		